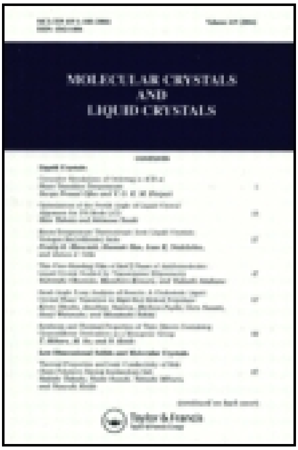

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Evidence for a Nematic Phase and "Memory Effect" in p-Methoxybenzylidene-p'-Propoxyaniline

Domenico Grasso [a]
[a] Istituto Dipartimentale di Chimica e Chimica Industriale dell'Università di Catania, Viale A. Doria, 8, 95125, Catania, (Italy)
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Evidence for a Nematic Phase and "Memory Effect" in *p*-Methoxybenzylidene-*p*'-Propoxyaniline

DOMENICO GRASSO

Istituto Dipartimentale di Chimica e Chimica Industriale dell'Università di Catania, Viale A. Doria, 8, 95125 Catania (Italy)

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A nematic phase has been evidenced for the title compound. A "memory effect" has been suggested.

As reported in a previous note,[1] we have begun a systematic study of the thermodynamic parameters of compounds which are derivatives of benzylideneaniline, to contribute to clarification of their mesomorphic behavior. To do this, the Thermal Microscopy technique (TM) is used along with Differential Scanning Calorimetry (DSC) measurements.

In studying the thermal characteristics of the title compound, we have noted an unusual behavior, unreported in the literature.

First of all, it is necessary to distinguish whether the solid sample used in the TM measurements was obtained by solidification of the corresponding liquid (solid A), or by crystallization from anhydrous ethanol (solid B). A different thermal behavior is shown, in fact, depending on the previous history of the compound. To clarify that, about fifty thermal cycles were carried out on several different samples. In every case, on heating the sample, a melting point at 119°C is found for the solid-isotropic liquid transition.

On cooling this isotropic liquid, a different behavior is evident, according to the solid compound used. Using the solid A, as sample, when we cool its isotropic liquid always the solid-isotropic, transition occurs and no mesophases are evident. Reheating the solid just formed, again the isotropic liquid is formed, and so on. If this thermic cycle (a) is repeated several times the overcooling reduce and the solidification temperature seems increase toward a limiting value. (Figure 1)

Using the solid B as sample, when we cool its isotropic liquid, a nematic phase appears at 98°C. This nematic phase on heating, melts to give the isotropic liquid at about the same temperature. On cooling, the nematic phase appears again, and so on the following cycles (b).

On strongly cooling the mesophase, a solid is formed roughly at about 65–70 C, that, if reheated, runs over again the previous cycle (a).

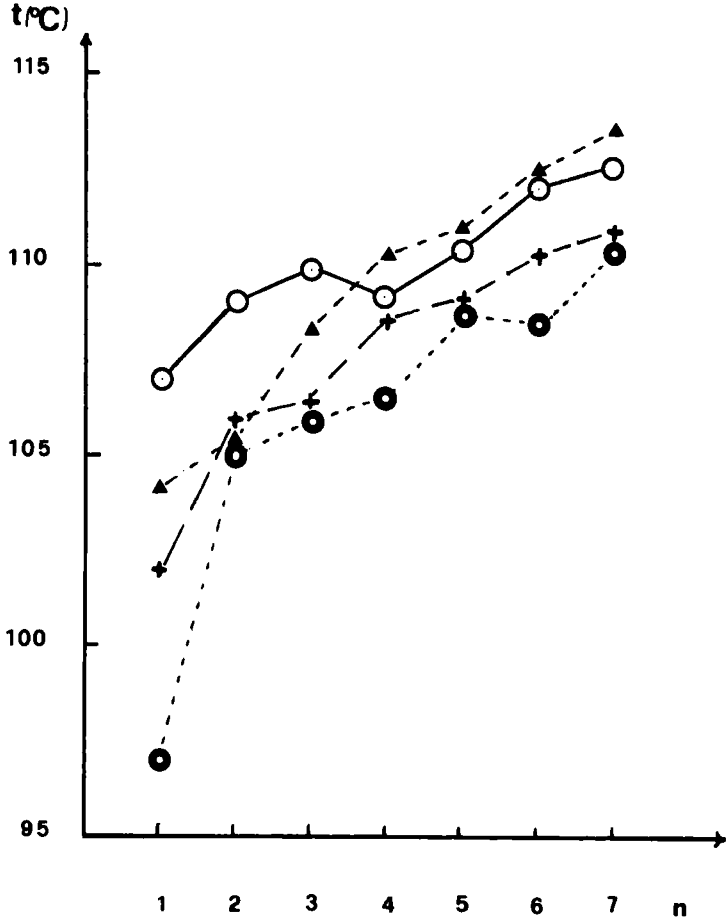
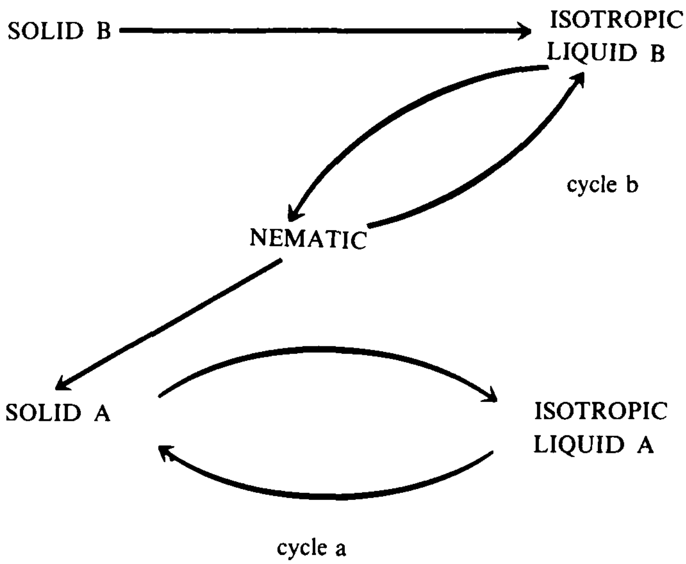


FIGURE 1 Solidification temperatures obtained by thermal microscopy measurements of isotropic liquid A, against number of thermal cycles.
Different symbols correspond to different sets of measurements on different samples.



An analysis of the experimental data suggests the following considerations:

i) the existence of a nematic phase;

ii) a different behavior of the solids A, and B;

iii) a different behavior of the "isotropic liquids" corresponding to solids A and B.

The "annealing time" in the isotropic phases corresponding to solids A and B, about 2 min., is probably not sufficient time for equilibration, to give the same result on cooling; thus the effect seen is a "kinetic" one. Simply heating to the isotropic phase briefly does not insure that one is dealing with the thermodinamically favored isotropic arrangement. As Griffin[2] has pointed out, there are two factors to be considered when discussing transitions among various phases: (a) thermodinamic stability of the phases, and (b) accessibility of one phase from its precursor phase. The observation of an unusual behavior of mesomorphic compounds, with apparition of new phases in relation to the previous thermal history of the compound has been reported by Lydon and Kessler.[3]

In conclusion it seems that the "isotropic liquid" B, unlike the A one, "remembers" a few order existing in the solid B, and by cooling it is able to give a nematic phase. Moreover, the fact that by subsequent transformations the solid A can be obtained from the solid B, excludes all possibility of doubt of an effect of purity on the behavior of solid B.

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